EVALUATION OF COAL TAR PITCH FRACTIONS AS FEEDSTOCKS FOR THERMALLY STABLE JET FUEL

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INTRODUCTION

Coal tar pitch, a by-product from the metallurgical coke industry, is made up of the volatile compounds evolved during coal carbonization. The inherent cyclic structure content indicates its ability to be upgraded into hydroaromatic and cycloalkane compounds that have been shown to contribute towards high fuel stability at elevated temperature [1,2,3]. Since 1960s coal tar pitch fractions have been successfully demonstrated to be a suitable feedstock for the production of jet fuels for high Mach aircraft [1,4], and have also been included in full-scale demonstrations in French fighter aircraft [5].

For the future development of high-performance jet aircraft flying at high Mach speeds, the fuel specifications have to be increased significantly due to the extreme operating conditions the fuel mat experience. The fuel may potentially be used as a heat sink in some parts of the aircraft and operated at temperature as high as 900°F. Under these conditions the fuel is stressed to temperatures above its thermal stability, which in turn leads to fuel degradation and coke formation [6,7]. It has been found that high thermal stability hydroaromatic and cycloalkane compounds are desirable components for advanced jet fuels [1,2,3]. As a result, coal tar pitch distillates, which can be converted to those structures under hydrotreatment process, are chosen again for jet fuel production. However, current evaluations on coal tar production have shown that the production of raw coal tar in the US has declined significantly over the past 30 years due to the environmental issues. But, by incorporating with suitable petroleum refinery streams, the feasibility and desirability of coal tar blending as a viable route for the production of thermally stable jet fuel would increase. Thus, we would need to protect and extend the lifetime of coal tar as a resource for advanced thermally stable jet fuel production.

The blends of various coal tar pitch distillates and suitable refinery streams have undergone laboratory-scale catalytic hydrotreatment. Coal tar pitch streams – high quinoline insolubles and low quinoline insolubles, carbon black oil, creosote oil, naphthalene still residue (NSR) and refined chemical oil (RCO) – and refinery streams – kerosene and light cycle oils (LCO) – were selected. The majority of these were eliminated early on in the study because of poor processing ability. Difficulties arising from asphaltene and pre-asphaltene precipitation from the heavy fraction were the main cause. The problems included a loss in catalytic activity and a decrease in hetero-atom removal. However, RCO proved to be an excellent feedstock. RCO is a very narrow boiling fraction, which contains over 50 % naphthalene. The hydrogenated products from the blends of RCO and LCO have produced good jet fuel fraction yields and high tetralin production – tetralin has been shown to have high thermal stability. Variations in reaction condition, pressure and temperature, as well as catalyst used have been performed to maximize the jet fuel fraction yield and tetralin conversion.

EXPERIMENTAL

Analysis Performed. Ultimate analysis of carbon, hydrogen and nitrogen compositions are obtained from a LECO CHN-600 analyzer and a LECO SC-132 sulfur determination analyzer. The feedstocks and products were analyzed by high temperature simulated distillation (HT-SimDis) GC analysis using a Hewlett-Packard 5890 series II plus fitted with a Restek MXT-500 SimDis column. The boiling point distribution and the cut point of 200-260°C fraction, jet fuel range, were observed. Quantitative analysis and chemical specification were performed on the feeds and samples using a Hewlett Packard 5890 GC fitted with a 5971 mass selective detector (MSD) fitted with a J+W DB17 capillary column. The analysis of feedstocks is shown in Table 1.

Catalyst Preparation. $NiMo/Al_2O_3$ and $NiMoP/Al_2O_3$ catalysts from Criterion have been employed for this work. The catalysts were presulfided following the method used by Ueda and co-workers [8].

Sample Used. Refined chemical oil (RCO) was obtained from Koppers Industries Company. British Petroleum (BP) supplied light cycle oils (LCO): LCO[a] light cycle oil feed, LCO[b] hydrogenated light cycle oil and LCO[c] deeply hydrogenated light cycle oil.

Methods for Hydrogenation. Hydrogenation experiments were performed in 25 ml microautoclave reactors following the methods used by Reddy *et al* [9]. The conditions for hydrogenation experiments included pressures between 500-1300 psig H_2 and temperatures between 325-375°C. Variations in the feedstock blending composition (LCO: RCO = 3:1, 1:1, 1:3 and 0:1) were assessed as well as the effect of the two catalysts, NiMo/Al$_2$O$_3$ and NiMoP/Al$_2$O$_3$. After collecting a small part of the reaction products from the reactor, the remainder was recovered with THF followed by filtration.

RESULTS AND DISCUSSION

First, we compared the basic blends between different LCOs (LCO[a], LCO[b] and LCO[c]) and RCO at varying compositions and catalysts, and under the baseline conditions. Figure 1 shows that the blend of different LCO with RCO gave different jet fuel yields. LCO[c] blends gave the outstanding jet fuel yield whereas those of LCO[a] and LCO[b] were in the same low-range yield. This is mainly due to the presence of hydroaromatic compounds in the LCO[c] that contribute to the higher conversion of the RCO through hydrogen donation and shuttling reactions.

The blending compositions of LCO[c]: RCO also affected the jet fuel yield (see Figure 1). By increasing the RCO concentration and using the NiMoP/Al$_2$O$_3$ catalyst, we see an increase in the proportion of the sample boiling in the jet fuel fraction (200-260 °C). This is due in part to the increase in tetralin in the products, through the composition of high boiling material and subsequent hydrogenation. Tetralin conversion, during RCO hydrogenation using NiMOP/Al$_2$O$_3$ catalyst (see Table 1) was lower than those of 1:1 blends under baseline condition in Table 2. Therefore, there was some synergistic effect promoted by the blend of LCO[c] and RCO. This again was probably due the hydrogen donation reactions.

Figures 2-3 show chromatograms of blends of LCO[c] and RCO before and after hydrogenation. The conversion of a significant portion of the naphthalene to tetralin can be seen along with the formation of other products. For an indication of the tetralin conversion, the calculated value was based on saturation of naphthalene ring only. Therefore, the actual value would be higher due to the contribution of the tetralin from the decomposition and hydrogenation of the high boiling point compounds. Furthermore, other cyclic structures in jet yield fraction of LCO[c] also play an important role in the production of potentially thermally stable compounds. Therefore, to optimize jet fuel yield, tetralin production and other thermal stable components, we need to blend RCO with LCO[c] with RCO loadings greater than 50%.

In addition, the hydrogenation conditions have formed products that have shown great increases in the H/C ratio and effective removal of sulfur and nitrogen. Table 2 shows the analyses of hydrogenated products by varying pressure, temperature and catalyst used. The H/C ratio of hydrogenated products has been increased and their colors become lighter as the increase of temperature. Sulfur and nitrogen content were decreased more than 80% and 70% respectively. This result shows that the catalysts, especially NiMOP/Al$_2$O$_3$, have worked well in both desulfurization and denitrogenation reactions.

Figure 4-5 shows the effects of pressure and temperature on tetralin conversion and jet fuel yield with the use of NiMo/Al$_2$O$_3$. Increases in temperature greatly affected both tetralin production and jet yield. The effect of pressure shows that conversion to tetralin and the fraction boiling in the jet fuel range goes through a maximum around the baseline conditions of 1000 psig. For the reactions at high temperatures, cracking of heteroatoms and large aromatic compounds and the

$$\text{(naphthalene)} + 2H_2 \xrightarrow[\triangle]{\text{catalyst}} \text{(tetralin)} \tag{1}$$
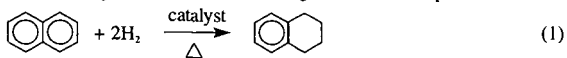
saturation of naphthalene molecules are more likely to occur. But at low-pressure condition, the reaction tends to shift chemical equilibrium to the right (Equation 1). This is why tetralin conversion is less likely to occur.

High-pressure condition also hindered the tetralin production as well as jet yield. Thus, it can be summarized that 1000 psig H_2 and 350-375 °C is the most suitable condition for hydrogenation of LCO[c]: RCO blends.

CONCLUSIONS

The blend of LCO^c and RCO under appropriate catalytic hydrogenation reaction can produce high quantities of tetralin, which indicates the potential high thermal stability, and an increase of sample boiling in the jet fuel fraction. The balance between jet fuel fraction yield, tetralin conversion and the production of other potentially thermally stable cyclic structures and can be controlled by blending composition and reaction conditions. The catalyst used plays an important role in tetralin conversion, desulfurization and denitrogenation processes.

ACKNOWLEDGEMENTS

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Table 1: Ultimate analyses of LCO (a-c) and RCO.

Feed	% C	% H	% N	%S	H/C ratio	Jet range (200-260 °C)
LCO^a	90.0	10.8	0.14	<0.05	1.44	18.5
LCO^b	88.8	11.3	0.12	<0.05	1.53	28.8
LCO^c	83.8	14.0	0.36	<0.05	2.00	32.5
RCO	91.7	6.5	0.43	0.42	0.84	52.1

Table 2: Analyses of hydrogenated products from refined chemical oil (RCO) and deeply hydrotreated light cycle oil (LCO) under varying conditions.

| Reaction condition	NiMo				NiMoP			
	H/C ratio	%N	%S	%Tetralin Conversion	H/C ratio	%N	%S	%Tetralin Conversion
LCO: RCO = 1:1 at 1000 psig H$_2$								
325°C	1.50	0.12	0.042	57.0	1.50	0.13	0.053	63.1
350°C (baseline)	1.51	0.09	0.041	67.7	1.61	0.07	0.034	73.8
375°C	1.56	0.12	0.040	80.8	1.69	0.03	0.021	81.7
LCO: RCO = 1:1 at 350°C								
500 psig	1.47	0.13	0.011	63.9	1.54	0.08	0.017	74.6
1000 psig (baseline)	1.51	0.09	0.041	67.7	1.61	0.07	0.034	73.8
1300 psig	1.67	0.13	0.069	56.3	1.56	0.12	0.061	57.6
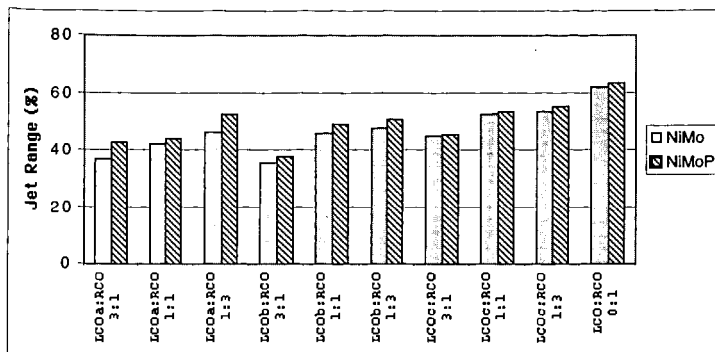
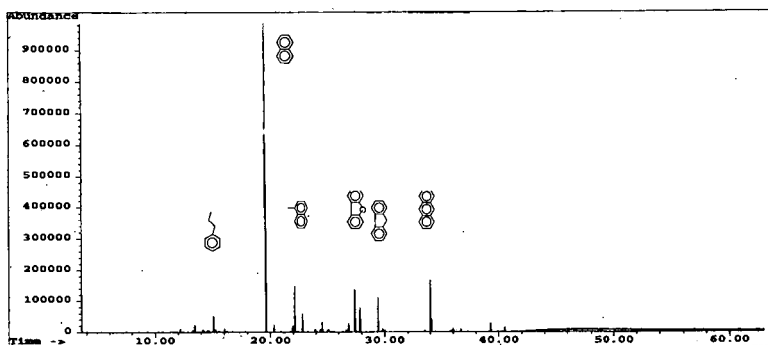Figure 1: The effects of variation of blending types and composition on jet fuel yield.

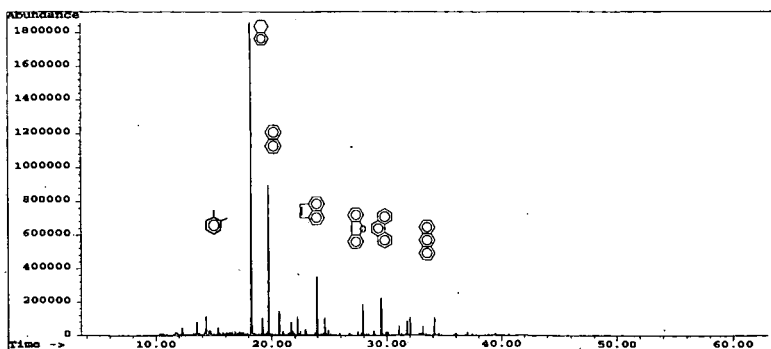Figure 2: GC trace of the blend of LCO^c and RCO before hydrogenation reaction.

Figure 3: GC trace of hydrogenated product from the blend of LCO^c and RCO after hydrogenation at 50°C, 1000 psig H_2 by using $NiMo/Al_2O_3$).
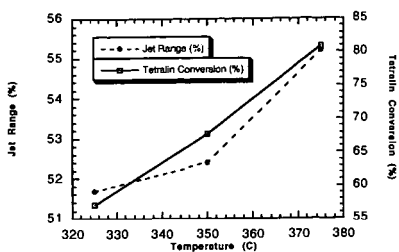
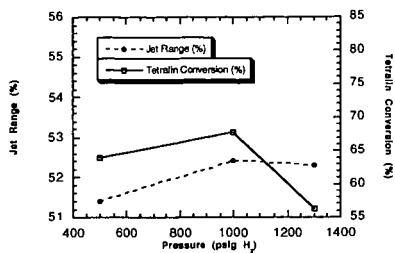Figure 4: Temperature effects on jet fuel yield and tetralin conversion.

Figure 5: Pressure effects on jet fuel yield and tetralin conversion.

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